

APPENDIX E

**BAY-DELTA DRINKING
WATER QUALITY:
BROMIDE ION (Br^-) AND
FORMATION OF BROMINATED
DISINFECTION BY-PRODUCTS**



**Bay-Delta Drinking Water Quality: Bromide Ion (Br⁻)
and Formation of Brominated Disinfection By-Products (DBPs)**

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Summary

This report is an outgrowth of a meeting involving an expert panel on bromide ion (Br^-), convened by the CALFED Bay-Delta Program in Sacramento, California on September 8 – 9, 1998. Experts (the authors of this report) on water chemistry, drinking water treatment, health effects, drinking water regulations, and source assessment and management held a public meeting to exchange information with utility, government, and environmental representatives in the presence of CALFED staff. Panel members were provided background reports and unpublished data both before and after the meeting. The purpose of this report is to provide CALFED with input on controlling concentrations of bromide ion (Br^-) within regions of the Sacramento River Delta-San Francisco Bay (i.e., the *Bay-Delta*) used as a source for drinking water supply.

The Bay-Delta region is a complex, multi-use system comprised of two major freshwater inflows (the Sacramento and San Joaquin Rivers), San Francisco Bay, and transitional estuarine and Delta areas. The primary export facility for drinking water is the State Water Project (SWP), which originates in the southern reaches of the Delta; other export points include the North Bay Aqueduct (NBA), the South Bay Aqueduct (SBA), and the Contra Costa Canal (CCC). CALFED has proposed three alternatives for managing the flow of Sacramento River water through the Delta to points of drinking water export; each of these alternatives, embodying channel modifications, storage, and possibly a new conveyance channel, will have varying effects on Br^- levels in exported water.

It is well known that disinfection by-products (DBPs) are formed during water treatment disinfection/oxidation. The impetus for this report is that, in the presence of Br^- and natural organic matter (NOM, measured as total organic carbon (TOC)), various brominated DBPs are formed including: brominated trihalomethanes (THMs) and haloacetic acids (HAAs), formed upon chlorination; and bromate ion (BrO_3^-), formed upon ozonation.

The major source of Br^- within the Delta is seawater derived through tidal exchange with San Francisco Bay. The major incremental source of TOC (beyond that associated with inflows) are agricultural drains situated throughout the Delta.

There are major concerns about the public health (e.g., carcinogenic, mutagenic, or reproductive) effects of DBPs in drinking water. Brominated DBPs such as

bromodichloromethane (a THM species) and BrO_3^- may be of particular concern. The U.S. EPA intends to promulgate more stringent drinking water regulations in November of 1998, limiting the maximum contaminant levels of THMs (sum of four species), HAAs (sum of five species), and BrO_3^- . EPA is also considering further DBP regulation and more stringent disinfection regulations (e.g., *Cryptosporidium* inactivation) which could further influence changes in disinfection practice and create a potential conflict between minimizing chemical (DBPs) and microbial risk.

There are very limited treatment options (i.e., membranes) for removing Br^- . Conversely, there are both conventional (coagulation, sedimentation, filtration) and advanced (granular activated carbon, membranes) processes for effective removal of TOC; however, these processes increase the ratio of Br^-/TOC and may not proportionally reduce chemical risk to public health. Options exist for minimizing bromate formation during ozonation (e.g., low-pH ozonation), or for removing BrO_3^- after its formation (e.g., chemical reduction with ferrous salts); however, there are water quality and technology-development constraints to their implementation (e.g., low pH ozonation for high-alkalinity source waters; substitution of ferrous salts for traditional coagulants). Management of Br^- may be best realized through a combination of treatment and source control, with the three CALFED alternatives reflecting different options for managing the intermixing of seawater with freshwater as it is conveyed through the Delta. Given the synergistic behavior of Br^- and TOC in forming DBPs, the co-occurrence within the Delta and the fate through treatment of both Br^- and TOC are of importance. Similarly, the co-occurrence of fecal contamination with these parameters can exacerbate the control options for DBPs because of potentially higher disinfection levels needed to control pathogens.

There must be both a short-term (before implementation of an alternative) and a long-term (after alternative implementation) strategy for drinking water utilities using Delta water. In the short-term, more emphasis should be placed on treatment with some possibilities for source control (e.g., treatment or rerouting of agricultural drainage or storage (external to Delta) for dampening variations in Br^- , possibly also lowering TOC, and limiting fecal contamination); in the long-term, more substantial source management options are possible with implementation of an alternative for conveying water through the Delta.

1.0 Introduction and Background

1.1 Significance of Bromide (Br^-) in Drinking Water Sources

Bromide ion (Br^-) occurs ubiquitously in natural waters, ranging from < 5 ug/L in some freshwaters to 65 mg/L (65,000 ug/L) in seawater. While it is considered a trace contaminant in drinking water supplies (i.e., usually < 1 mg/L or $< 1,000$ ug/L), Br^- can have a significant impact on drinking water quality. Bromide itself is harmless; however, it reacts with water-treatment chemical disinfectants and oxidants (e.g., chlorine and ozone) to form potentially harmful disinfection by-products (DBPs). Chemical disinfection reduces microbial risk from pathogenic microorganisms (e.g., *Giardia* and *Cryptosporidium*); however, the formation of DBPs (e.g., bromodichloromethane and bromate) poses a chemical risk to public health. While Br^- serves as the inorganic DBP precursor, it interacts with natural organic matter (NOM), measured as total organic carbon (TOC), playing the role of the organic DBP precursor, which contributes to the formation of organic DBPs.

1.2 General Sources and National Occurrence of Br^- and TOC

Both natural sources of bromide in water (e.g., geochemical weathering, connate seawater, seawater intrusion) and anthropogenic sources (e.g., industrial and oil field brine discharges) exist. A nation-wide survey (Amy, et al., 1994) reported that the average drinking water source in the U.S. contains 62 ug/L of bromide, with a range from 5 to 430 ug/L observed for 88 randomly-sampled sources; the 90-percentile concentration was estimated to be about 300 ug/L. The average Br^- concentration in 12 targeted (known high Br^- levels) sources was 210 ug/L (Bay-Delta water exported through the State Water Project (SWP) was included in this grouping).

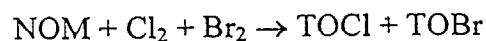
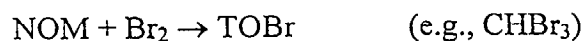
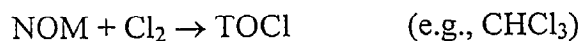
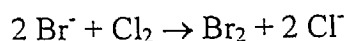
Amy et al. (1994) reported a nation-wide average TOC concentration in 100 drinking water sources to be 2.7 mg/L, a finding consistent with other studies; the range of TOC concentrations was <0.2 to 21 mg/L. The co-occurrence of TOC with Br^- can be represented by a Br^-/TOC ratio; the average ratio reported by Amy et al. (1994) was 28 ug $\text{Br}^-/\text{mg TOC}$; no significant correlation was observed between Br^- and TOC occurrence.

1.3 Formation and Chemistry of Brominated Disinfection By-Products (DBPs)

The traditional chemical disinfectant, chlorine (Cl_2), as well as alternative disinfectants, ozone (O_3), chlorine dioxide (ClO_2), and chloramines (NH_2Cl , monochloramine), all form their own suite of DBPs. The following discussion will emphasize chlorination and ozonation DBPs because of the importance of Br^- in their formation. In contrast, the major chlorine-dioxide DBP is chlorite ion (ClO_2^-), a non-brominated DBP. When chloramine practice involves free chlorine followed by ammonia addition, lesser amounts of chlorination DBPs are formed; however, observations of enhanced formation of cyanogen chloride have raised concerns about a possible bromine analog, cyanogen bromide.

1.3.1 Trihalomethanes (THMs) and Haloacetic Acids (HAAs)

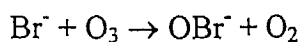
Bromide (Br^-) ion is itself harmless; however, through interaction with chemical disinfectants and oxidants, it can become incorporated into disinfection by-products (DBP). Br^- is oxidized by chlorine (Cl_2) to bromine (Br_2), more specifically hypobromous acid in equilibrium with hypobromite ($\text{HOBr} \leftrightarrow \text{H}^+ + \text{OBr}^-$). Cl_2 and Br_2 collectively react with natural organic matter (NOM), measured as total organic carbon (TOC), to form halogenated (chlorinated and/or brominated) organic DBPs that can be represented by organic-halogen (TOX) including organic-chlorine (TOCl) and organic-bromine (TOBr) components. Less than 50 % of the TOX pool has been identified as specific compounds/compound classes such as trihalomethanes (THMs) and haloacetic acids (HAAs). Of the four THM species, one is fully chlorinated (chloroform, CHCl_3), one is fully brominated (bromoform, CHBr_3), and two are mixed species (bromodichloromethane and dibromochloromethane). Of the nine HAA species, three are fully chlorinated (tri-, di-, and mono-chloroacetic acid), three are fully brominated (tri-, di-, and mono-bromoacetic acid), and three are mixed species (bromodichloro-, dibromochloro-, and bromochloro- acetic acid). The relevant chemistry is summarized below:



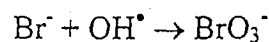
The formation of total THMs (TTHM) is positively (+) influenced by temperature, pH, Cl₂ dose, Br⁻ concentration, TOC, and reaction time. The formation of total HAAs (THAA) is similarly influenced by the same parameters except for pH; pH has a significant inverse (-) effect on certain HAA species (e.g., trichloroacetic acid). The relative amounts of Br⁻ and TOC affect the species distribution of both TTHM and THAA, with a higher Br⁻/TOC ratio driving the mixture toward greater bromination. NOM properties, as indicated by measurements of UV absorbance at 254 nm (UVA₂₅₄) and specific UV absorbance (SUVA = UVA₂₅₄/TOC), also affect TTHM and THAA formation. UVA₂₅₄ and SUVA are indicative of the aromatic (non-polar) character of NOM. A positive correlation have been observed between TTHM and SUVA. Polar NOM has been shown to be more influential in THAA than TTHM formation. Higher bromination (THM-Br and HAA-Br) has been observed for polar NOM. It is important to note that Br has a molecular weight of 80 versus 35.5 for Cl; thus, because of weight-based (ug/L) standards, Br⁻ exacerbates TTHM and THAA formation. Another important observation is that brominated DBPs form more rapidly than chlorinated DBPs, a factor that may affect control strategies such as chloramination involving free-chlorine contact subsequently followed by ammonia addition.

1.3.2 Bromate (BrO₃⁻) and Organic-Bromine (TOBr)

Br⁻ is also oxidized by ozone (O₃) to HOBr/OBr⁻ (Br₂); OBr⁻ serves as an important reaction intermediate to formation of bromate (BrO₃⁻), an inorganic DBP. BrO₃⁻ can form through two potential pathways: a molecular ozone (O₃) and a hydroxyl radical (OH[•]) pathway. The molecular ozone pathway is summarized below:



The OH[•] pathway is represented below, in a simplified (unbalanced) format:



Bromate is positively (+) affected by temperature, pH, O₃ dose, and Br⁻ concentration. The radical pathway is more dominant under higher pH conditions and in the presence of NOM.

TOBr may also form during ozonation in the presence of Br^- , with an inverse (-) pH effect, through the reaction of NOM with the HOBr intermediate:



1.3.3 Co-Occurrence of Br^- and TOC, DBP Mixtures, and Balancing Risk

The above discussion shows the linkage between Br^- , the inorganic DBP precursor, and NOM (TOC), the organic precursor. Thus, their co-occurrence in Delta water and their relative removals during water treatment are of concern. As regulations drive practice toward use of multiple disinfectants/oxidants, a DBP mixture will result. From a risk perspective, there is a need to balance chemical risk to public health, associated with the resultant DBP mixture created by a disinfectant/oxidant or combinations thereof, with microbial risk posed by pathogenic microorganisms.

Another important consideration is the co-occurrence of Br^- and TOC with microbes (e.g., fecal coliforms); the co-occurrence of Br^- and *Cryptosporidium* creates a dilemma between effective inactivation by ozone versus bromate formation.

1.4 National Occurrence of Brominated DBPs

Krasner et al. (1989) reported the results of a 35-utility DBP survey. All four THM species and five HAA species (HAA_5) were measured prior to point of entry into the distribution system. Median values for chloroform, bromodichloromethane, dibromochloromethane, and bromoform were reported to be 13, 6.6, 3.4, and 0.6 ug/L, respectively; median values for trichloroacetic acid, dichloroacetic acid, monochloroacetic acid, dibromoacetic acid, and monobromoacetic acid were reported to be 5.4, 6.4, 1.1, 1.2, and <0.5 ug/L, respectively. Recent work by Zhu (1994) has shown that, because of the concentration of bromochloroacetic acid (a sixth species), HAA_6 on average is about 10 % greater than HAA_5 . Little is known about the occurrence of the remaining three HAA species. Krasner et al. (1993) found bromate levels ranging from < 5 ug/L to 60 ug/L in pilot studies and at operating ozonation facilities.

1.5 The Bay-Delta System as a Drinking Water Source

The Bay-Delta system is a region encompassing the confluence of the Sacramento and San Joaquin Rivers, San Francisco Bay, and the transitional estuarine and Delta areas (Figures 1 and 2). CALFED is charged with developing a consensus on potentially conflicting beneficial uses of the Bay-Delta, with drinking water supply identified as one important beneficial use. CALFED has articulated three alternatives to reconcile Bay-Delta issues. These three alternatives, summarized below, would have varying impacts on drinking water quality in general, and levels of bromide ion (Br^-) in particular:

- Alternative 1 (Figure 3) “proposes existing Delta channels, with some modifications for water conveyance and various storage options”;
- Alternative 2 (Figure 4) “proposes significant modifications of Delta channels to increase water conveyance across the Delta combined with various storage options”; and
- Alternative 3 (Figure 5) “includes Delta channel modifications coupled with a conveyance channel that takes water around the Delta with various storage options”. (This alternative will include an isolated conveyance facility with a capacity of 8,000 to 12,000 cfs, connecting the Sacramento River to drinking water export facilities).

The average annual freshwater inflow into the Delta is about 27 MAF/yr (million acre-feet/year), 62 % derived from the Sacramento River. This inflow, however, is volumetrically small in comparison to tidal exchange with San Francisco Bay. On average, about 5.9 MAF/yr are exported via the major drinking water aqueduct, the State Water Project (SWP, 3.6 MAF/yr); and the major agricultural water aqueduct, the Central Valley Project (CVP, 2.3 MAF/yr). On a much smaller scale, drinking water is exported via the North Bay Aqueduct (NBA, 25,000 acre-feet/year), the South Bay Aqueduct (SBA, 160,000 acre-feet/year), and the Contra Costa Canal (CCC, 100,000 acre-feet/year). Flow patterns throughout the Delta are influenced by tidal actions and export operations. There is a clear seasonality to inflow, lowest in the summer and highest in the winter; this is in contrast to variations in water demand which are highest in summer. Variations in inflow versus demand can be dampened by storage in the form of surface reservoirs or groundwater basins; presently, there are 30 reservoirs with a combined capacity of 25 MAF.

FIGURE 1

